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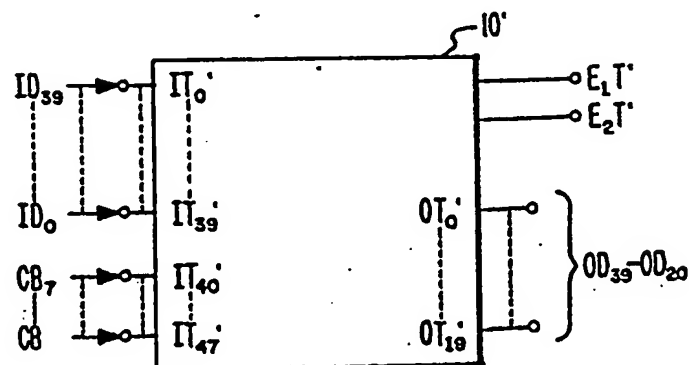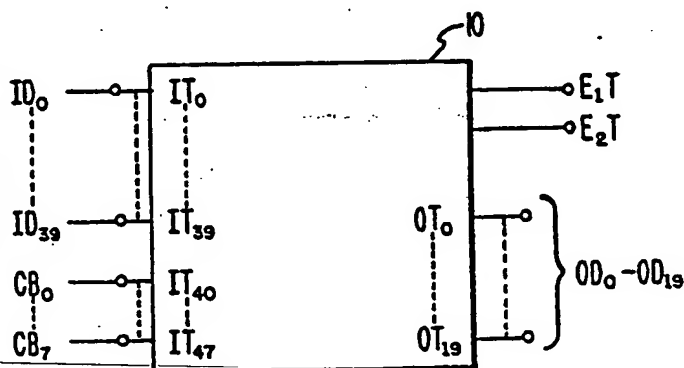
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(54) Title: LANGMUIR BLODGETT FILMS

(57) Abstract

Novel Langmuir-Blodgett (LB) films of ABAB structure in which the compounds A and B are different and contain complementary groups which result in non-centrosymmetry of the layer plane. Three types of structure are described (i) in which A and B have similar backbones with complementary chromophore groups (ii) in which A and B have similar backbones with complementary functional groups and (iii) in which A and B have related functional groups but complementary backbones. Preferred LB films contain the compound (I).

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LANGMUIR BLODGETT FILMS

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10   This invention relates to Langmuir-Blodgett (LB) films, and to
devices using such films.

An LB film is generally prepared by depositing a monolayer of a
surface-active material onto a water surface, using now well estab-
lished techniques.   The molecules of the surface active material
15   align in the monolayer, the hydrophilic ends remaining in the water,
and the hydrophobic end projecting out of the surface. By other
known techniques, this monolayer may be transferred essentially
intact onto the surface of a solid substrate, and further monolayers
deposited on the layer on the substrate to form a film, ie a
20   Langmuir-Blodgett film.

Compounds used in LB films are generally long chain molecules,
containing 14 or more carbon atoms in their chain, with a hydro-
philic "head" and a hydrophobic "tail", such as long chain car-
boxylic acids, eg $CH_3(CH_2)_{14}CO_2H$, where the CO_2H group constitutes
25   the hydrophilic head.

LB films have properties, which make them useful in certain
electronic devices.

Conventional (Y-type) LB films are symmetrical about their
layer planes; However one of the most interesting features of the
30 · LB technique is the ability it gives to carry out the assembly of
complicated molecular systems by depositing successive layers of
different materials[2]. In particular multilayer films of the
general type ABAB.. where A and B are monolayers of different
materials, and are non-centrosymmetric, are expected to show inte-
35   resting and potentially useful pyroelectric, piezoelectric and
second order non-linear optical eff cts. A two compartment LB
trough has been developed which allows the convenient fabrication of

ABAB.. films[3].

Int rest in pyroelectrics for thermal detectors is generally increasing because of their wide spectral response, sensitivity and lack of cooling requirements. Thin film pyroelectrics in particular are provoking much interest due to the shorter response times available with low thermal mass, large area capability, and compatibility with electronic readout devices such as the charge coupled device (CCD) or the pyro-FET. Being a low temperature technique the LB technique is compatible with semiconductor materials and large areas of uniform deposition are in principle possible.

To produce a pyroelectric effect a material must possess a spontaneous polarisation P_s (C cm^{-2}) thus it must also possess a polar axis. This requires that the material be non-centrosymmetric. Normally P_s is not directly observable due to compensation of the surface polarization charge by conduction charges from the material or atmospheric ions. However P_s may be a function of the temperature T, and if T is changed slightly the compensation charges are too slow (since pyroelectrics are dielectrics) to follow the change in P_s and a charge $\pm$ Q appears on the surfaces perpendicular to the polar axis; this is the pyroelectric effect.

We define the pyroelectric coefficient by

$$P = \underline{dP_s}/dT \text{ (C cm}^{-2} \text{ K}^{-1})$$

and therefore

$$Q = pdT$$

Generally p is also p(T) but the variation is normally weak except near phase transitions in ferroelectric pyroelectrics. Therefore we can write Q = pΔT where ΔT is a small change in T. Conventional high performance pyroelectrics have p = 3 x 10^{-8} C cm^{-2} K^{-1}. Nearly all such materials are ferroelectrics operating close to their Curie temperature to obtain the high dPs/dT.

In conventional Y-type LB films the molecular dipole moments of adjacent layers cancel and therefore P_s = 0.. In an ABAB ... film the dipole moments of A and B being different do not cancel but add vectorally to give a non zero P_s and a polar axis perpendicular to the film plane. X and Z type films will also show a non-zero Ps; pyroelectricity and pi zoelectricity in such films has been reported

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by Blinov[4,5].

It is an object of the present invention to provide novel LB films which have improved pyroelectric and piezoelectric properties. Other objects and advantages will be apparent from the
5   following description.

According to a first aspect of the invention a Langmuir-Blodgett film of ....ABAB..... structure is composed of compounds A and B which are different, A and B containing complementary groups that result in non-centrosymmetry of the layer plane, the layers of
10   A and B being optionally separated by a counter layer.

By "complementary groups" it is meant that A and B contain different atomic groupings in their structure so as to result in non-centrosymmetric layering in the LB film.

Compounds A and B will normally be long chain molecules con-
15   taining 14 or more carbon atoms, in an essentially linear skeleton, one end of the molecule being of generally hydrophilic character, the other being generallyhydrophobic.

In preferred embodiments of the invention, the compounds A and B may have the following general structural types (i), (ii) and (iii):
20   (i) Compounds A and B may have a generally similar backbone in terms of disposition of functional groups, the length of their backbone, their molecular shape and polarity, but wherein A and B contain groups which are chromophores, which may be the same or different, which result in non-centrosymmetric layering of A
25   and B in the LB film.

In one embodiment of this type, the chromophore group in A and B is the same   , but the group is disposed within their moecular structures rotated through 180° about an axis perpendicular to the molecular skeleton relative to the positions of the hydro-
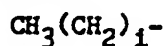30   philic and hydrophobic ends.

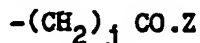For example A may have a structure:

E - C - F

and B may have a structure:

$E^1 - C^1 - F^1$
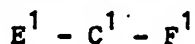
35   where E and E^1 may be the same or different, and are independently selected from:

$CH_3(CH_2)_i-$

4

where i is 2-20,

F and F^1 may be the same or different, and are independently selected from:

$$-(CH_2)_j \, CO.Z$$

where j is 0 to 10, preferably 2 to 4 and Z is selected from -OH, C_{1-6} alkyl and NR^1R^2 where R^1 and R^2 may independently be H or C_{1-6} alkyl. F is a hydrophilic group. E, E^1, F and F^1 may contain the same or different numbers of carbon atoms, in each case the total in E plus F and E^1 plus F^1 being 14 or more.

C and C^1 are chromophores which result in non-centrosymmetric layering of A and B in the LB film. C and C^1 may be the same or different, and are preferably selected from

$$X - \langle O \rangle - Y$$

where X and Y are each independently selected from:

$=NH, =NR^3$ (R^3 being C_{1-4} alkyl), $=CO, =CH(CN), =CH(ONO_2), =CH$(Halogen), $-COO-, -OOC-, =CH(ONO), -CO-NH-, -CO \ NR^4_-$ (where R^4 is C_{1-6} alkyl) and $-O-$.

It is preferred to use polar groups X and Y which undergo solid state reorganisation, to give a large dP_s/dT in the region of room temperature.

C and C^1 may respectively be $X - \langle O \rangle - Y$ and $Y - \langle O \rangle - X$ in the molecules A and B, ie to give structures of the type:

$$E - X - \langle O \rangle - Y - F$$

and

$$E' - Y - \langle O \rangle - X - F'$$
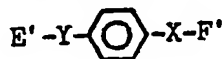
so that in these structures the chromophore is rotated through 180° relative to the positions of the hydrophilic and hydrophobic ends.

In LB films of the type (i) non-centrosymmetric layering occurs as below:

A	B	A	B
E - C - F	$F^1 - C^1 - E^1-$	E - C - F	$F^1 - C^1 - E^1$
E - C - F	$F^1 - C^1 - E^1-$	E - C - F	$F^1 - C^1 - E^1$
E - C - F	$F^1 - C^1 - E^1-$	E - C - F	$F^1 - C^1 - E^1$
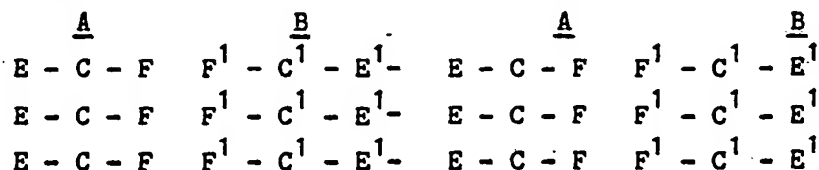
(the layer planes here being shown as running vertically)

In LB films of type (i), if it is considered necessary to

interpose one or more counter-layers between the layers AB, a pref rr-
ed material for counter-layers is a long chain alkyl amine f formula
$CH_3(CH_2)_nNH_2$ where n is 16 to 26, preferably 18 to 20.

A particularly preferred chromophore group is

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$$-\overset{O}{\underset{\|}{C}}-\langle O \rangle-\overset{CH_3}{\underset{|}{N}}-$$

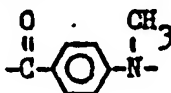(ii) Compounds A and B may have a generally similar backbone in
terms of the length of their backbone, their molecular shape
and polarity, but in which A and B contain different complementary
10 functional groups which result in non-centrosymmetric layering in
the LB film.

The functional groups which result in non-centrosymmetric
layering are preferably located at the terminal position of the
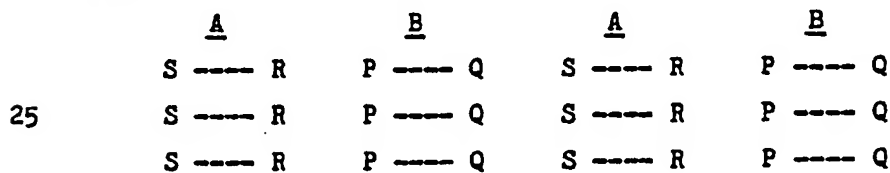molecule.

15   For example A may be a molecule:

R ———— S

and B may be a molecule:

P ———— Q

where R and P may be the same of different functional groups or
20 hydrophobic termini, and Q and S are different functional groups,
———— representing the molecular backbone, non-centrosymmetric layer-
ing in the LB film occurs as below:

<u>A</u>	<u>B</u>	<u>A</u>	<u>B</u>
S ———— R	P ———— Q	S ———— R	P ———— Q
S ———— R	P ———— Q	S ———— R	P ———— Q
S ———— R	P ———— Q	S ———— R	P ———— Q

25

(the layer planes being shown as running vertically)

Various preferred embodiments of this
type are discussed below:

30 (a) A is a long chain alkyl amine of the structure $C_n H_{2n+1} \cdot NH_2$
where n is an integer between 16 and 26, preferably 18 to 20.   It
has been found that at n greater than 24 the chain begins to become
too rigid for use at room temperatures, and that at n less than 16
the amine becomes too soluble in the subphase.

35   B is a long chain fatty acid of the structure $R^5 (CH_2)_m COOH$
where R^5 is selected from CH_3 and $CH_2=CH$, and where m is indepen-

6

dantly an integer within the limits and preferences set above for n.

(b) A is a long chain alkyl amine as defined in (ii)(a) above, and B is a compound of general structure:

$$CH_3(CH_2)_k-X-\langle O \rangle-Y-(CH_2)_l-COZ$$
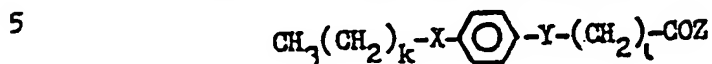
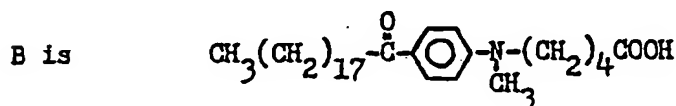in which k is 2 to 20, l is 0 to 10 preferably 4, X, Y and Z are as defined in connection with type (i) above.

An example of such an A-B combination is

A is stearylamine (n-octadecylamine $C_{18}H_{37}-NH_2$)

$$CH_3(CH_2)_{17}-\overset{O}{\overset{\|}{C}}-\langle O \rangle-\underset{CH_3}{N}-(CH_2)_4COOH$$

B is

(c) A is a long chain alkyl amine as defined in (ii)(a) above, and B is a compound of the structure:

$$CH_3(CH_2)_p-N \langle \rangle = \langle \rangle = O$$
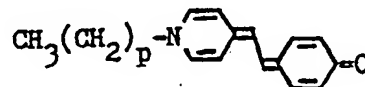
where p is 6 to 25, preferably no more than 21.

(iii) Compounds A and B may have the same or a closely related functional group and different complementary structural backbones which result in non - centrosymmetric layering in the -ABAB- film.

The functional group is preferably located at a terminal position in the molecule. A preferred functional group is -COZ, with Z as defined above, especially -OH ie a carboxylic acid group. One or more of the compounds A and B may contain a chromophore, such as

$$-X-\langle O \rangle-Y-$$

where X and Y are as defined above.

In a preferred LB film of this type:

A is a long - chain alkyl carboxylic acid of general formula:

$$R^5-(CH_2)_m-COOH$$
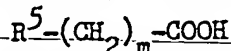
where R^5 and m are as defined above, and

B is a chromophore - containing compound of general formula:

$$CH_3(CH_2)_k-X-\langle O \rangle-Y-(CH_2)_l-COZ$$

where k, X, Y, l and Z are as defined above.

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In this description the term "chromophore" is used as that part of a molecule which produces its colour, or its light absorbance in the non visible region of the spectrum. Preferred chromophores are polar chromophores, as it is polarity of the chromophore which is
5 responsible for their pyroelectric activity in LB films rather than their light absorbance.

Langmuir Blodgett films according to the invention show pyro-electric activity in the region of room temperature. Some may also show piezoelectric behaviour. Films according to the invention
10 which have a high degree of polarisable structure may also show non-linear optical properties.

Films according to the invention also have the advantage that their polarisation is solidly built into their structure, and is thus unlikely to be lost or reversed at an electric field strength
15 below the dielectric breakdown field.

Langmuir Blodgett films according to the invention may be prepared by known means, for example using the apparatus and method described in reference 3.

Films according to the invention may be used in electro optical
20 and other electronic devices which use a Langmuir Blodgett film as a sensing element, and therefore according to a further aspect of the invention an electronic device is provided which incorporates a Langmuir Blodgett film as described above as its sensing element. In particular there is provided a thermal sensor which incorporates
25 as its sensing element a Langmuir Blodgett film according to the invention. Such devices may be constructed using methods known in the art.

8

The invention will now be described by way of example only with reference to the accompanying figures 1 to 4, which show:

Fig.1   Voltage responsivity versus chopping frequency
5   for ...ABAB... LB film of stearylamine /ω -
           tricosenic acid. Total thickness 500 layers.

Figs. 2, 3, 4   Pyroelectric coefficient (p) versus absolute
           temperature ($^{\circ}$K) for various LB films of types
           (i), (ii)(a), (ii)(b) and (iii).

10

Experimental Details

1.   Materials

Saturated carboxylic acids were obtained from Sigma (99%).
15   Stearylamine (n-octadecylamine) was obtained from ICN Pharmaceu-
ticals Inc.   ω-tricosenoic acid ($CH_2=CH(CH_2)_{20}COOH$) was kindly
supplied by Dr A Barraud and A Ruaudel-Teixier (CEN Saclay) and
Gedye$_{22}$ was kindly supplied by Dr G L Gaines Jr., (General Electric
Company).   All the above were used without further purification.
20   The dye called 18ON4A was synthesised using a standard method.   All
the materials were spread from high purity solvents (BDH Ltd Aristar
grade) usually 1,1,1, trichloroethane or chloroform.

Gedye$_{22}$ is an abreviation for the compound:

25   $$CH_3(CH_2)_{21}-N\langle\underset{=}{\rangle}=\langle\underset{=}{\rangle}=\langle\underset{=}{\rangle}=0$$

30

9

180N4A is an abrviation for the compound:

$$CH_3(CH_2)_{17}-\overset{\overset{O}{\|}}{C}-\langle O \rangle-\underset{\underset{CH_3}{|}}{N}-(CH_2)_4COOH$$
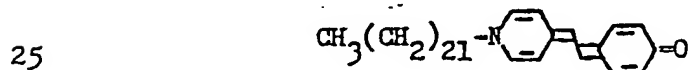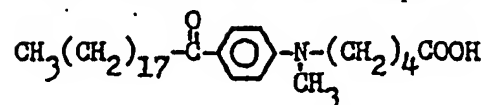
Other compounds were synthesised as described below.

5   <u>Compounds of the general formula:</u>

$$CH_3(CH_2)_m-O-\langle O \rangle-\overset{\overset{O}{\|}}{C}-(CH_2)_nCOOH \qquad \underline{Class\ 1}$$

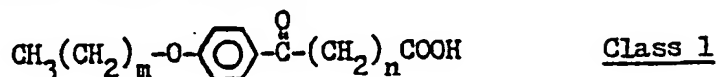(a)   Phenol (0.1 mole) and sodium hydroxide (0.1 mole) in ethanol

10 (100 ml) were stirred and refluxed during the dropwise addition of
an appropriate 1-bromo alkane (0.095 mole), stirring and refluxing
being continued until the 1-bromo alkane was consumed, as evidenced
by TLC (typically 12 hr) after removal of the ethanol solvent, the
reaction mixture was diluted with water and the product extracted

15 with chloroform. The dried extract was vacuum evaporated and the
residue crystallised from light petroleum to give the phenoxy alkane
(Yield ca. 80%).

(b)   Aluminium·chloride (0.03 mole) was added to a solution of the
above phenoxy alkane (0.01 mole) and the methyl ester chloride of

20 the appropriate alkane dioic acid (0.0105 mole) in dichloromethane
(20 ml). The mixture was stirred at room temperature for 24 hr or
until TLC showed the absnece of starting material, then hydrolysed
with dilute hydrochloric acid and ice. Chloroform extraction and
vacuum evaporation gave the keto-ester which was recrystallised from

25 light petroleum (Yield ca. 80%).

(c)   The above keto-ester (0.01 mole) was refluxed with sodium
hydroxide (0.04 mole) in ethanol (15 ml.) and water (2 ml.), until
TLC showed the absence of starting material (ca.1hr). After removal
of the solvent ethanol the product was collected by chloroform

30 extraction. Concentration of the dried extract gave the ketoacid
which was further purified by recrystallisation from chloroform.

<u>Compounds of the general formula:</u>

$$CH_3(CH_2)_n-\overset{\overset{O}{\|}}{C}-\langle O \rangle-O-(CH_2)_mCOOH \qquad \underline{Class\ 2}$$
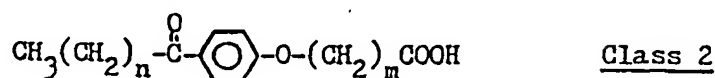
35

(a)   w-Phenoxyalkanoic esters. The requisite w-bromalkanoic acid
ester was made by stirring the commercially available acid (2g.)

with the appropriate alcohol (70 ml.) at room temperature, the
reaction being catalysed by the addition of a small amount of acetyl
chloride. After 24 hr., or when TLC indicated total conversion, the
excess alcohol was removed by vacuum distillation and the ester

5 taken up in chloroform. The extract was washed with sodium bicar-
bonate, water, then dried and vacuum evaporated to give the ester
which was used directly without further purification. Alkylation of
phenol with the w-bromoester was carried out as in 1(a) above using
the same alcohol as solvent as was used in the previous esterifi-

10 cation step to avoid trans-esterification.

(b)   Acylation of w-phenoxyalkanoic esters. The requisite acyl
chlorides were prepared from commercially available alkanoic acids
by reaction with thionyl chloride, and purified by vacuum distill-
ation. The acylation reaction was carried out using the method

15 outlined in 1(b) above, the resulting ketoester being hydrolysed to
the w-(4-alkanoylphenoxy) alkanoic acid by the method of 1(c)
.above.

Compounds of the general formula:

20 $$CH_3(CH_2)_m-\overset{\overset{O}{\|}}{C}-\underset{}{\bigcirc}-\underset{\underset{CH_3}{|}}{N}-(CH_2)_nCOOH$$ Class 3
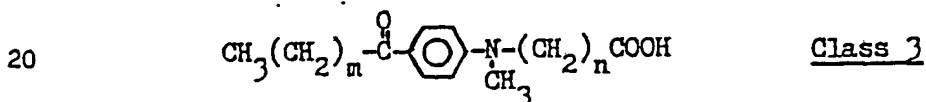
(a)   w-(N-methyl-N-phenylamino) alkanoic esters. A mixture of
N-methylaniline (0.1 mole), the methyl or ethyl w-bromoalkanoate of
2(a) above (0.1 mole), and sodium carbonate (0.3 mole) in hexa-

25 methylphosphorus triamide (50 ml.) was stirred and heated at 140°C
until TLC showed total conversion of starting material (ca. 20 hr.),
then cooled and diluted with water (200 ml.). The precipitated acid
was collected, washed, and recrystallised from ethanol. Acids which
precipitated as oils were collected by chloroform extraction prior

30 to recrystallisation.

(b)   w-N-(4-formylphenyl)-N-methylamino alkanoic esters. The
aminoester from (a) (0.005 mole) was added to phosphorus oxychloride
(5 ml.) in N,N-dimethylformamide (20 ml.) at room temperature. The
mixture was heated at 90-95°C for 2 hr., then cooled and neutralised

35 with aqueous sodium hydroxide. The crude aldehydic ester was
collected by extraction with ethyl acetate and purified by chromato-
graphy over silica in ethyl acetate - light petroleum, prior to

recrystallisation from light petroleum (Yield ca. 75%).

(c)   A solution of Grignard Reagent was prepared from the requisit
alkyl halide (0.006 mole) and magnesium turnings in dry tetrahydro-
furan (30 ml.) under argon. The above aldehydic ester (0.004 mole)
5   in dry tetrahydrofuran (5 ml.) was cooled to -15°C and the solution
of Grignard reagent added dropwise during 10 min. The reaction
mixture was stirred at -15 - -5°C until TLC showed no further
conversion (ca. 45 min), then hydrolysed with aqueous ammonium
chloride and extracted with ether. Evaporation of the dried
10   ethereal extracts and chromatography of the residue over silica in
ethyl acetate - light petroleum gave the alcohol (ca. 55%) which was
oxidised directly.

(d)   The above alcohol in dichloromethane (5 ml.) was treated with
pyridinium dichromate (0.014 mole) and stirred at 0°C for 12 hr.
15   The reaction mixture was diluted with water and the ketoester
collected by ether extraction. It was purified by chromatography
over silica with ethyl acetate - light petroleum (Yield ca. 30%).

(e)   The ketoester (0.003 mole) was refluxed with sodium hydroxide
(0.009 mole) in ethanol (18 ml.) and water (2 ml.) until reaction
20   was complete as determined by TLC. On cooling, the solution was
acidifed with dilute hydrochloric acid. The precipitated ketoacid
was collected, washed and recrystallised from chloroform (Yield
ca.70%).

Using the methods described above, compounds as follows
25   were prepared:

	$\underline{m}$	$\underline{n}$
Class 1	8	4
"	11	4
"	15	4
"	15	2
Class 2	17	4
Class 3	17	4
"	17	6
"	17	8

(line 30 marks the "15 2" row; line 35 marks "Multilayer Deposition")

35   2.   Multilayer Deposition

All films were deposited on aluminized glass cover slips cut to
2 cm square. The cover slips were cleaned ultrasonically in Decon-

90 followed by rinsing in pure filtered water and drying in a stream of nitrogen before evaporation of the 1 cm wide aluminium electrode stripe (> 60nm thickness) in a cryogenically pumped (oil free) vacuum coater. Thickness control was achieved by use of a quartz

5 crystal monitor at the substrate plane. The source was a resistively heated tungsten filament and the source to substrate distance was 40 cm.

Stearylamine/carboxylic acid ABAB... films were produced using the RSRE two-compartment trough[3]. Each compartment was maintained

10 at a surface pressure of 30 mN m^{-1} over a subphase of pure water (original resistivity 18 MΩ cm). Transfer to the substrates was effected at$\sim$ 5mm sec^{-1} with the amine being deposited on the down stroke. Transfer ratios were near unity.

Stearylamine/Gedye$_{22}$ films were deposited with the surface

15 pressure in the Gedye compartment being 25 mN m^{-1}. The subphase contained 10^{-3}M ammonium sulphate and was maintained at a pH of 7.5 $\pm$ 0.3. Transfer was effected at $\sim$ 1 cm min^{-1} to allow the Gedye film to drain. Stearylamine was transferred on the down stroke.

Stearylamine/18ON4A films were deposited under identical

20 conditions to the stearylamine/carboxylic acid films.

In all cases two substrates were coated together. After deposition the films were left for 24 hrs before evaporation of a top aluminium electrode stripe perpendicular to the first. The final device area was 1 cm^2.

25 3. Preliminary Film Assessment

    (a) Infrared spectroscopy

        Infrared spectra were obtained using a Perkin Elmer 983G infrared spectrometer. The samples were deposited as films 50 layers thick on the polished faces of Ge prisms (5 x 1.5 x 0.2

30   cm, Harrick Scientific Corp) and the measurement was made using the technique of attenuated total reflection (ATR)[6].

    (b) Dielectric Measurement

        Capacitance and tan δ data were obtained using a Hewlett-Packard 4274ALCR meter. The signal amplitude was set at

35   50 mV. All measurements were made in laboratory ambient conditions on the samples assessed for pyroelectric activity.

    (c) X-ray d-spacings

13

Measurements were made on a 50 layer ABAB film of stearyl-amine / arichidic acid deposited on a silanized unaluminized cover slip. A low - angle diffractometer with Cu K radiation was used.

5   4. Pryoelectric Assessment.

This was carried out using dynamic and static methods as described in G W Smith, M F Daniel, J W Barton and N Ratcliffe, Proc. Conf. on Langmuir Blodgett Films, Schenectady NY, July 1 - 4 1985, in Thin Solid Films (TSF ref. 8560).

10   Results

1. Infrared Spectra.

The results indicated the formation of the ions $C_{19}H_{39}COO^-$ and $C_{18}H_{37}NH_3^+$ due to proton transfer between the acid and the amine. The 'salt' of these two ions has therefore been formed,

15 with a large dipole moment.

2. Pyroelectric Measurements.

The static method was found to allow determination of temper-ature changes more accurately and results are summarised briefly in Table 1.

20   In Table 1 the following values are given:

d   = X-Ray d- spacings

ε_r = dielectric constant

tan δ

p   = pyroelectric coefficient

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Since P_s is dipole moment/unit volume and since the hydrocarbon tails of the saturated fatty acids contribute to the molecular volume but not significantly to the dipole moment we attempted to introduce a systematic variation in P_s and hence hopefully in p by

5 varying the length of the fatty acid B layers in our films. It is obvious from Table 1 that this objective has not been achieved. Calculation yields an expected change in P_S of 15% on going from C_{18} acid to C_{24} acid and this small change, if it appears at all in p, is lost in the scatter of the results. All the amine/saturated

10 acid films give p $\sim$ 5 x 10^{-11} C.cm^{-2}.K^{-1}.

Films of stearylamine with the unsaturated fatty acid ω-tricosenic acid consistently gave values twice as high p $= 1$ x 10^{-10}C. cm^{-2}.K^{-1}. This presumably reflects the temperature dependence of the dipole moment of the terminal double bond (0.3 D) since that

15 is the only difference between ω-tricosenoic acid and saturated carboxylic acids.

Films incorporating the merocyanine dye Gedye$_{22}$ gave very low values of p (8 x 10^{-12} C cm^{-2} K^{-1}). These films when measured had the dye in its yellow form[2] with the enolic oxygen

20 protonated, which reduces the intramolecular charge transfer contribution to the dipole moment. Also there is no amine/acid salt formation. So P_s for these films may be small compared with the amine/acid films and this may explain the small value of p. The higher value for ϵr is an indication of the high polarisability of

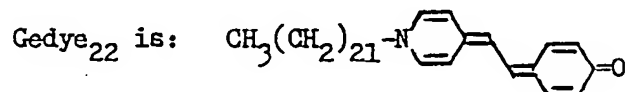25 the chromophore which has possibilities for non-linear optics.

Also included in Table 1 for comparison are the data obtained for a Y-type film of ω-tricosenoic acid showing the very small observed pyroelectric effect in a centrosymmetric LB film which may be due to small differences in the transfer ratios in the up and

30 down directions or residual drift in the apparatus.

The temperature dependence of p for ABAB... films of stearylamine with various fatty acids is shown in Figure 2. The low
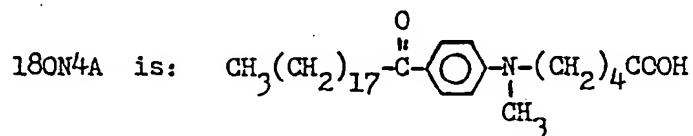
15

Table 1.

A	B	d (μm)	ε_r (1kHz)	tan δ	$p(Ccm^{-2}K^{-1})$ (280-285K)
$CH_2CH(CH_2)_{20}COOH$	$CH_2CH(CH_2)_{20}COOH$	0.45	2.85	0.0007	2×10^{-12} *
$C_{18}H_{37}NH_2$	$C_{17}H_{35}COOH$	0.26	2.71	0.016	3.2×10^{-11}
..	$C_{19}H_{39}COOH$	0.13	2.48	0.020	5.8×10^{-11}
..	$C_{21}H_{43}COOH$	0.23	2.82	0.033	3.3×10^{-11}
..	$C_{23}H_{47}COOH$	0.15	2.66	0.009	6.0×10^{-11}
..	$Gedye_{22}$	0.23	6.49	0.04	8.1×10^{-12}
..	$18ON4A$	0.14	3.24	0.006	2.25×10^{-10}
..	$CH_2CH(CH_2)_{20}COOH$	0.40	2.91	0.094	1.14×10^{-10}

$Gedye_{22}$ is: $CH_3(CH_2)_{21}-N$⟨=⟩$=$⟨=⟩$=O$

$18ON4A$ is: $CH_3(CH_2)_{17}-\overset{O}{\overset{\|}{C}}-$⟨◯⟩$-\underset{CH_3}{N}-(CH_2)_4COOH$

* Y-type film for comparison.

temperature limit was determined by the cooler and the high temper-
ature limit by the background current, which varied from film to
film but always increased sharply above room temperature. it is
obvious that p increases at higher temperatures with the rate of
increase being much higher above about 280K. Below that temperature
all three curves are quite parallel. This general trend of p(T) was
found for all films examined.

X-RAY MEASUREMENTS

The bilayer repeat distance for a 50 layer film of stearylamine
arachidic acid has been determined to be 49 $\overset{o}{A}$. This is somewhat
smaller than the value one would calculate from measuring molecular
models (54 $\overset{o}{A}$) and indicates a degree of molecular tilt within the
layer planes.

DISCUSSION

By making certain assumptions it is possible to calculate an
approximate maximum value of P_s for the amine/acid films. Assum-
ing complete proton transfer, a resulting charge separation of 0.3
nm and a bi-molecular (acid + amine) volume of 1.25 x 10^{-27} m^3
we obtain $Ps = 4$ μC cm^{-2}. The observed values for p therefore
represent a change in P_s of $\sim$ 10 ppm K^{-1}. It is interesting to
note that the calculated value for P_s is similar to that measured
for the high performance pyroelectric TGS (triglycine sulphate)[9]
(2.7 μC cm^{-2}). The greater than 500 fold difference in p is
therefore even more striking. However TGS is ferroelectric which
means that its polarisation can be switched by a sufficiently high
field applied for long enough and that its polarisation vanishes
above its Curie temperature by a crystallographic rearrangement.
For an ABAB... film the polarisation is solidly built into the
structure and one cannot conceive of any electric field short of the
dielectric breakdown field which could change that. Similarly no
temperature below the melting point is likely to change P_s signi-
ficantly. The low values of p are thus explained by the fact that
the charge on the headgroups is probably invariant with temperature
and the only change in P_s is due to a change in molecular volume
due to thermal expansion.

Films containing the 18 ON 4A dye will have larger values of P_s
than stearylamine/fatty acid films because the dipole moment of the

chromophore is in the same sense to that at the head group. The
higher observed value of p then probably means one of two things.
Either the dipole moment or the orientation of the chromophore within
the films changes thus changing the projection of its dipole moment
5   on the polar axis (film normal) and its contribution to P_s. We
cannot as yet decide between these two options.

In all the films so far examined the effect of increasing the
temperature is to decrease P_s.

CONCLUSIONS

10   We have succeeded in producing ABAB... films of stearlyamine
with various film forming materials. As expected these films
exhibit pyroelectric acivity and we have meaured this as a function
of temperature and material. Calculation of P_s for the amine/fatty
acid films yields a surprisingly high value which is not refelected
15   in p. Films containing 18 ON 4A, display a larger value for p. It
thus appears that much can be done to increase p by introducing
polar groups with the right characteristics.

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In a further series of experiments, LB films of types (iii) and (i) above were prepared and investigated. These contained the compounds:

18ON4A   (see above)

18NO4A $CH_3(CH_2)_{17}N$-⟨O⟩-$\overset{\overset{CH_3}{|}}{}$ $\overset{\overset{O}{||}}{C}.(CH_2)_4COOH$

14O' O4A $CH_3(CH_2)_{13}O$-⟨O⟩-$\overset{\overset{O}{||}}{C}.(CH_2)_4COOH$

Eicosanoic acid $CH_3(CH_2)_{18}COOH$

Experimental Method.

The compounds were repeatedly recrystallised and their purity checked by thin layer chromatography and mass spectroscopy.

Dilute solutions (0.2 - 1.0 mg/ml) in 'Aristar' (BDH Ltd, UK) grade solvents were spread on a commercial two compartment trough incorporating the RSRE gate design as described above. Pressure was maintained at $\pm$ 1 mN m^{-1} of the set transfer pressure for each material. The subphase conditions were pH = 8.5 ± 0.2; Cd^{2+} = 2.5 x 10^{-4}M. The subphase had an original resisitivity of 18 M O cm. Substrate speeds of 1mm/sec were used. 18ON4A was normally dipped on the up stroke, 14O' O4A and 18NO4A on the up stroke. Eicosanoic acid could be dipped on either stroke. The substrates and electrode arrangement was as described above.

Pyroelectric coefficients and dipole moments were determined by known techniques (ref. 10 and 11). An ambient of dry nitrogen gas was used throughout.

Results.

(1) Type (iii) Films.

Results are given in Table 2 below, and graphically in Fig 4. The sign of the pyroelectric current was the same in all three films. Cooling produced a current from the bottom to the top electrode, therefore Ps increases with decreasing temperature. Reversing the deposition order for the 18ON4A / eicosanoic acid film reversed the direction of current flow. p increased with temperature for most of the films.

Table 2

A	B	μ (x10^{-9}Cm)	bilayer rep. dist.	tilt^o	Ps (x10^{-3}Cm^{-2})	p (x10^{-7})
eicosanoic acid	14O' O4A	1.2±0.3	5.52nm	28.9	7.9	1.6
..	18ON4A	1.9	5.4nm	43	9.3	1.9

note: tilt = tilt of chromophore containing group B with
respect to film normal.

In these films use of 18ON4A is thus shown to give better
Ps and p.

(2) Type (i) films.

Two different structures of type (i) containing a chromo-
phore in each layer have been prepared, ie:

|	A	B
	14O' O4A	18ON4A
and	18NO4A	18ON4A

The results for these two films are shown in Fig. 3.

The pyroelectric response of 14O' O4A / 18ON4A was about
twice that of 18NO4A / 18ON4A.

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    Plenum 1971.

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CLAIMS

1.   A Langmuir-Blodgett (LB) film of ABAB structure composed of compounds A and B which are different and which contain complementary groups that result in non-centrosymmetry of the layer plane the layers A and B optionally being separated by a counter-layer.

2.   An LB film according to claim 1, characterised in that compounds A and B have a generally similar backbone in terms of disposition of functional groups, length, molecular shape and polarity and in which A and B contain chromophores, which may be the same or different, which result in non-centrosymmetric layering of A and B in the layer plane.

3.   An LB film according to claim 2, characterised in that the chromophore group in A and B is the same, but the group is disposed within the molecular structures of A and B rotated through 180° about an axis perpendicular to the molecular skeleton relative to the positions of the hydrophilic and hydrophobic ends.

4.   An LB film according to claim 3, characterised in that A and B are independently selected from compounds having a structure:

$$CH_3(CH_2)_i-X-\langle\bigcirc\rangle-Y-(CH_2)_jCOZ$$
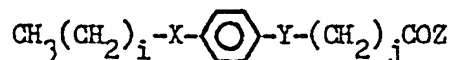
where i is 2-20, j is 1-10, z is selected from -OH, C_{1-6} alkyl and NR^1R^2 where R^1 and R^2 may independently be H or C_{1-6} alkyl, and where X and Y are independently selected from =NH =NR^3 (R^3 being C_{1-4} alkyl), =CO, =CH·CN , = $CHONO_2$, = $CH(Halogen)$, -COO-, -OOC-, = $CH(ONO)_2$ - CO-NH-, - CO.NR^4 (where R^4 is C_1 - C_6 alkyl) and -O- .

5.   An LB film according to claim 1, characterised in that A is a long chain alkyl amine of structure $C_nH(2n+1)-NH_2$ where n is 16-26, and B is a long chain fatty acid of structure $R^5-(CH_2)_m-COOH$ where R^5 is selected from CH_3 and CH_2=CH and where m is 16-26.

6.   An LB film according to claim, characterised in that A is a long chain alkyl amine of structure $C_nH(2n+1)-NH_2$ where n is 16-26, and B is a compound of general structure:

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$$CH_3(CH_2)-X-\langle O \rangle-Y-(CH_2)_1 COZ$$
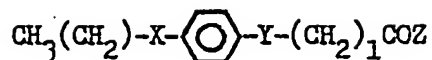
in which k is 2-20, l is 0 to 10, and Y and Z are as defined in claim 4.7

7.   An LB film according to claim 1 characterised in that A is a long chain alkyl amine of structure $C_nH(2n+1)NH_2$ where n is 16-26, and B is a compound of structure:

$$CH_3(CH_2)_p-N\langle = \rangle = \langle = \rangle =O$$
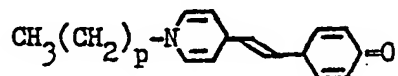
where p is 6-25.

8.   An LB film according to claim 1, characterised in that A is a long chain carboxylic acid of general formula $R^5(CH_2)_m COOH$ where R^5 and m are as defined in claim 5 and B is a compound of general formula:
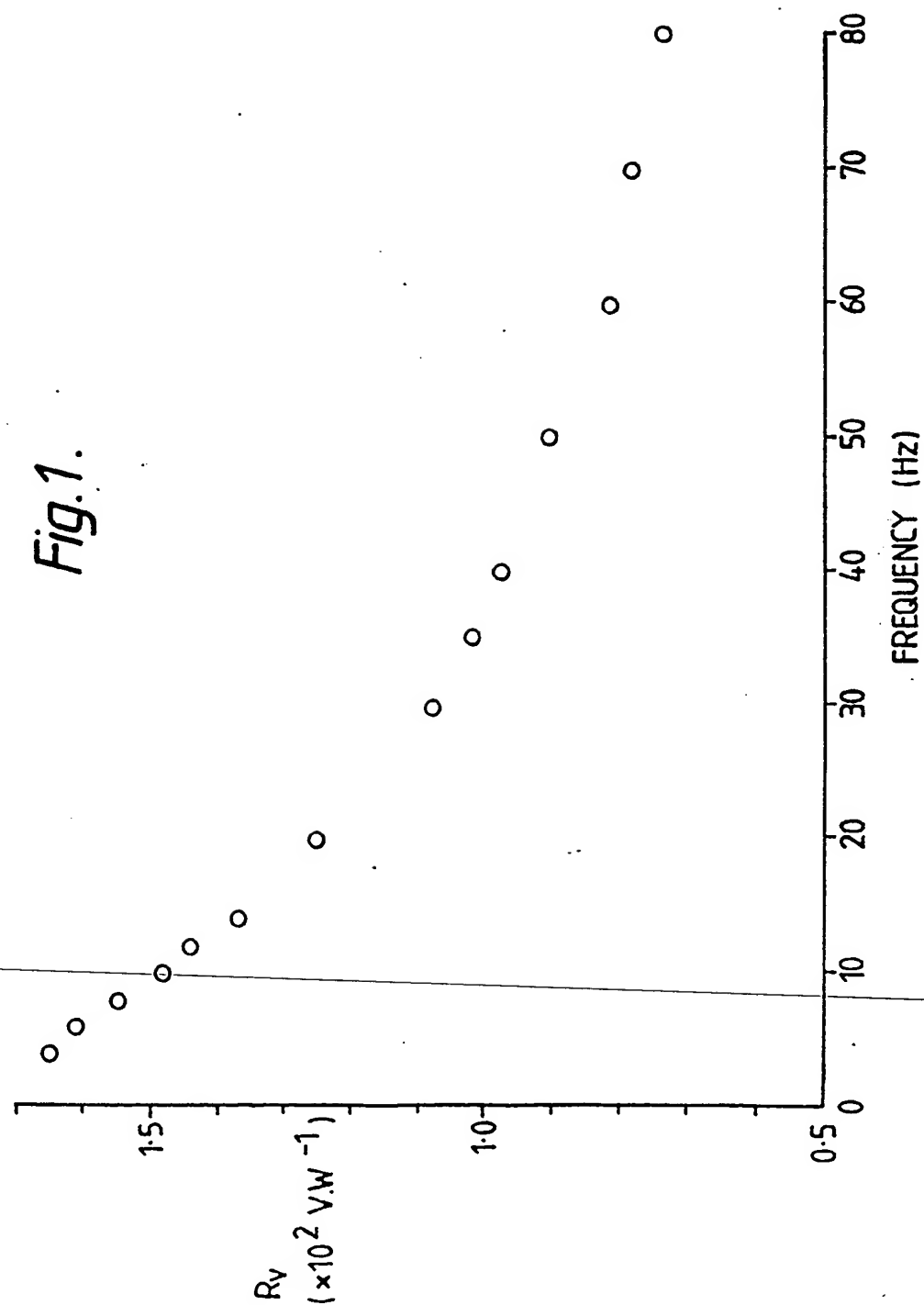
$$CH_3(CH_2)_k-X-\langle O \rangle-Y-(CH_2)_1 COZ$$

where k is 2-20, l is 0 to 10 and X, Y and Z are as defined in claim 4.

9.   An LB film according to any one of claims 4, 6, or 8, in which X is $=CO$ and Y is $=N(CH_3)$ or X is $=N(CH_3)$ and Y is $=CO$.

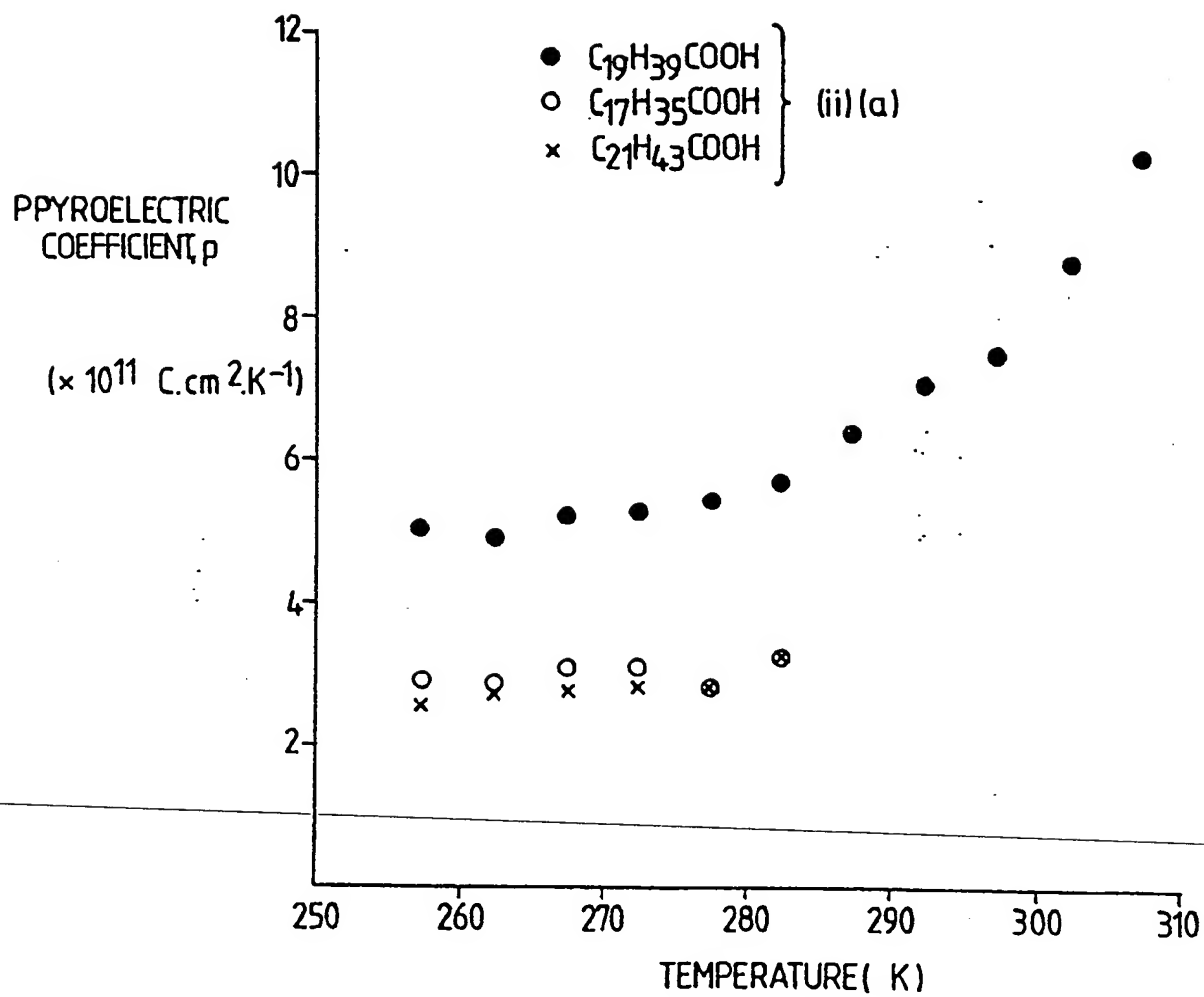10.   An electro optical device incorporating an LB film according to any one of the preceding claims.
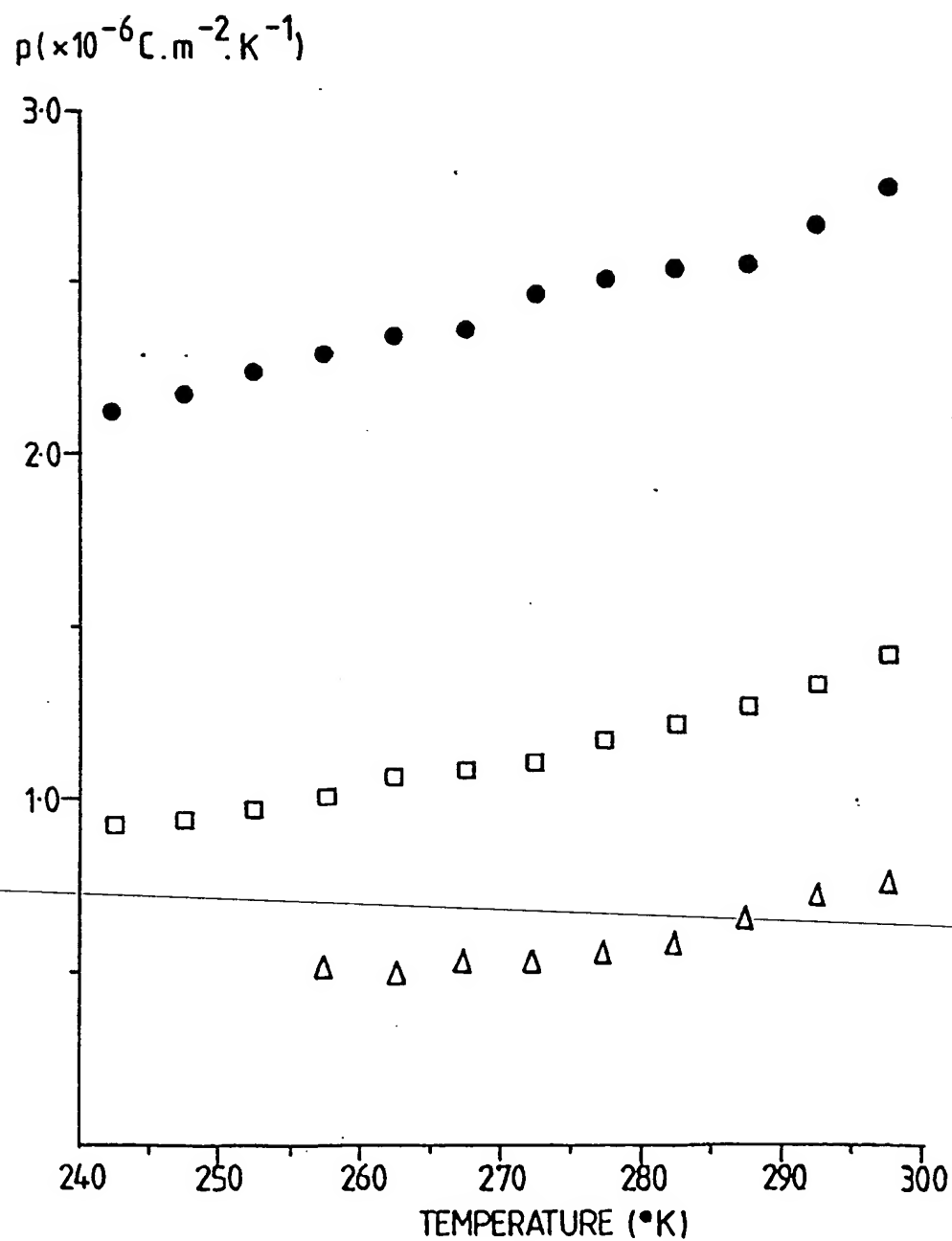
Fig.1.

Fig.2.

Legend:
- ● $C_{19}H_{39}COOH$
- ○ $C_{17}H_{35}COOH$ } (ii)(a)
- × $C_{21}H_{43}COOH$

PPYROELECTRIC
COEFFICIENT, p

$(\times 10^{11}$ $C.cm^{2}.K^{-1})$

TEMPERATURE(K)

Fig.3.

● 180N4A / 140'04A   (i)

□ 180N4A / 18N04A   (i)

△ eicosanoic acid / stearylamine. (ii)(a)

Fig.4.

● 180N4A / stearylamine   (ii)(b)
○ 180N4A /eicosanoic acid   (iii)
□ 18NO4A/eicosanoic acid   (iii)
△ 140'04A/eicosanoic acid   (iii)
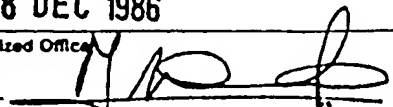
$p(\times 10^{-6} C.m^{-2}.K^{-1})$

TEMPERATURE (°K)
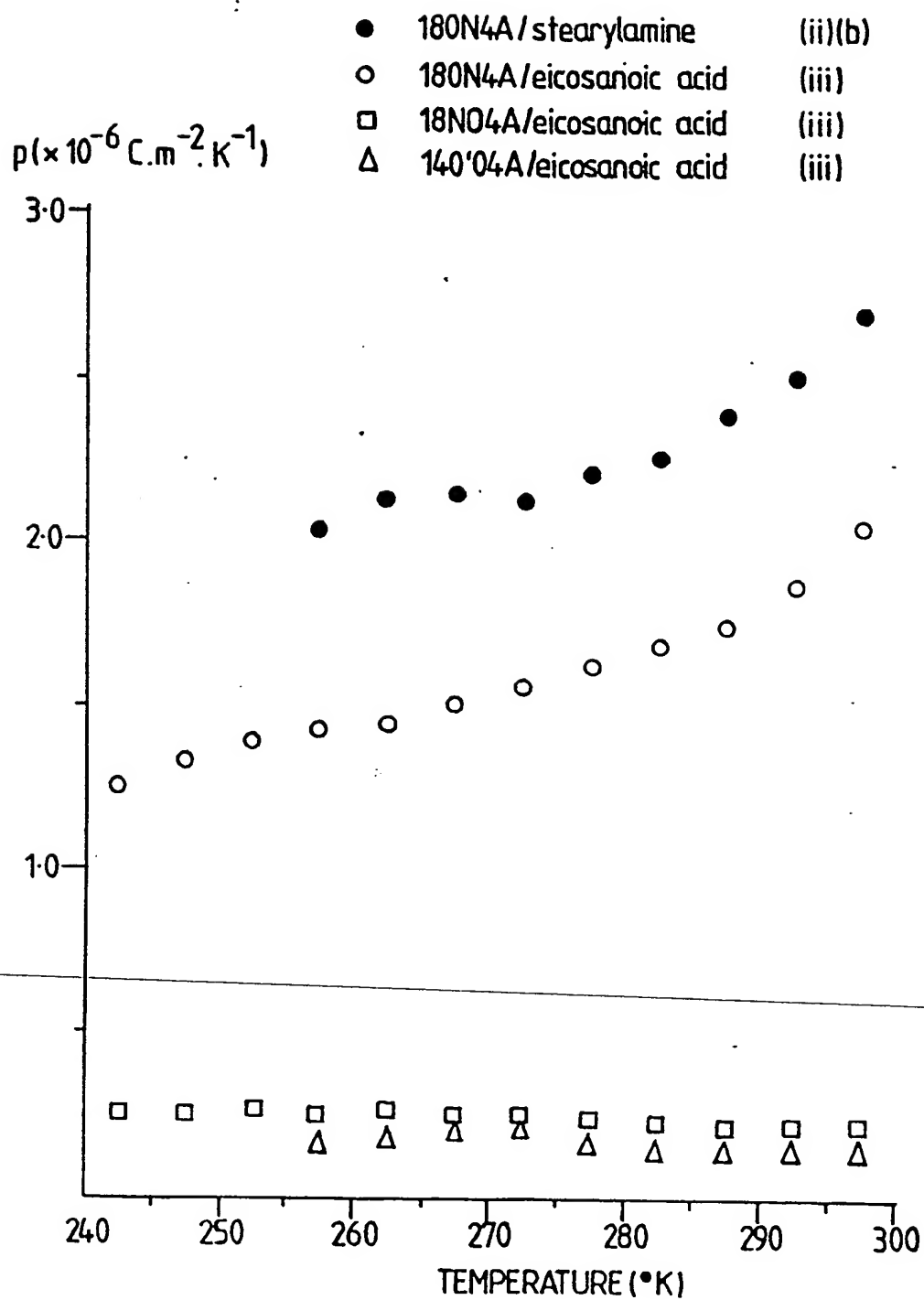
INTERNATIONAL SEARCH REPORT

International Application No **PCT/GB 86/00371**

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) *

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC^4: H 01 L 29/28; H 01 L 37/02; H 01 L 41/18; G 02 F 1/37

II. FIELDS SEARCHED

Minimum Documentation Searched *

Classification System	Classification Symbols
IPC^4	H 01 L; G 02 F

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched *

III. DOCUMENTS CONSIDERED TO BE RELEVANT *

Category *	Citation of Document, ** with indication, where appropriate, of the relevant passages 12	Relevant to Claim No. 13
X	Molecular Crystals and Liquid Crystals and Letters, volume 102, no. 617, 1984 (New York, US), M.F. Daniel et al.: "Preparation of non-centrosymmetric langmuir-blodgett films with alternating merocyanine and stearylamine layers", pages 193-198 see page 194, last paragraph - page 195, paragraph 2; page 197, paragraph 2 - page 198, paragraph 2 (cited in the application)	1,7
X	Thin Solid Films, volume 115, no. 1, May 1984, (Lausanne, CH), I.R. Girling et al.: "A method for the preparation of an alternating multilayer film", pages 85-88 see page 85, paragraph 2; page 86, paragraph 3 - page 87, paragraph 1; figure 5	1,2
A	Thin Solid Films, volume 120, 1984, (Lausanne, CH), L.M. Blinov et al.: "Polar langmuir-blodgett films", pages 161-170 see page 161, paragraph 1 - page 163, paragraph 1 (cited in the application)	1,4

* Special categories of cited documents: 10

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IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
10 November 1986	**18 DEC 1986**

International Searching Authority	Signature of Authorized Officer
EUROPEAN PATENT OFFICE	M. VAN MOL

Form PCT/ISA/210 (second sheet) (January 1985)

III. DOCUMENTS CONSIDERED T BE RELEVANT (CONTINUED FR M THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
A	EP, A, 0081477 (UNIVERSITY PATENTS INC.) 15 June 1983 see page 12, lines 1-21; page 40, lines 1-19; claims 1-3; figure 1 --------	

This Annex lists the patent family members relating to the
patent documents cited in the above-mentioned international
search report. The members are as contained in the European
Patent Office EDP file on 25/11/86

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Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A- 0081477	15/06/83	EP-A,B	0021695	07/01/81
		EP-A,B	0022618	21/01/81
		JP-A-	56042229	20/04/81
		JP-A-	56043220	21/04/81
		AU-A-	5895880	08/01/81
		AU-A-	5903580	08/01/81
		EP-A,B	0077577	27/04/83
		CA-A-	1158598	13/12/83
		US-A-	4431263	14/02/84
		AU-B-	541737	17/01/85
		AU-B-	546234	22/08/85
		CA-A-	1203541	22/04/86
		US-A-	4581315	08/04/86
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		US-A-	4536450	20/08/85